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EXCITED-STATE ENERGETICS AND DYNAMICS OF LARGE
MOLECULES COMPLEXES AND CLUSTERS(U) TEL-AVIV UNIV
(ISRAEL) DEPT OF CHEMISTRY J JORTNER ET AL

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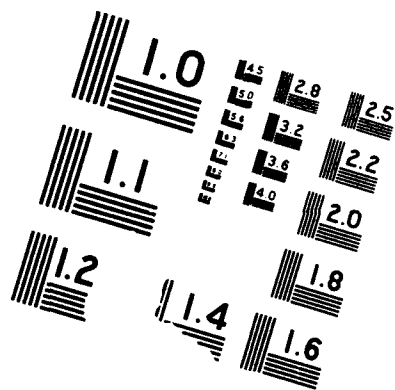
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PROGRESS REPORT FOR THE PERIOD MAY 1, 1986 - OCTOBER 30, 1986

4th Periodic Report

1. Title: EXCITED-STATE ENERGETICS AND DYNAMICS OF LARGE MOLECULES, COMPLEXES AND CLUSTERS
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6. PROGRESS IN TECHNICAL APPROACH

New techniques for spectroscopy in supersonic expansions and in the development of specific supersonic sources were developed.

6.A Vacuum Ultraviolet Absorption Spectroscopy in Supersonic Expansions. We have combined the techniques of vacuum ultraviolet (VUV) spectroscopy together with planar supersonic jets, which allows for the interrogation of absorption spectra of large molecules cooled in supersonic expansions in the near VUV region. The experimental setup consists of a high pressure Xe lamp, CaF_2 optics, a vacuum ultraviolet spectrograph and a nozzle slit (0.27x90 mm, repetition rate 9 Hz and gas pulse duration 300 μsec). The characteristics of this spectroscopic setup are: (i) Energy range 6-10 eV. (ii) Spectral resolution 0.1 Å. (iii) Routine measurements of high-energy absorption spectra. (iv) Interrogation of fluorescence excitation spectra of the parent molecule or its photoproducts with limiting quantum yields of $Y \geq 10^{-4}$.

6.B Development of Conical Nozzles for Supersonic Jets. Conical nozzles (nozzle opening angle $\theta = 30^\circ$, and nozzle diameter $D = 0.3$ mm) were constructed and used in conjunction with a magnetic pulsed valve. The use of conical nozzles considerably enhances clustering in supersonic expansions, facilitating studies of large van der Waals complexes and clusters.

7. ACCOMPLISHMENTS OF OBJECTIVES

7.A Energetics of Rydberg States of Jet Cooled Molecules. VUV absorption spectra of benzene, benzene- D_6 and naphthalene cooled in planar supersonic expansions were measured over the range 2000-1600 Å, providing evidence on energetics, line broadening and interference effects.

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- 7.B Rydberg States of Anthracene. Several Rydberg transitions of jet-cooled anthracene were observed in the spectral region 1900-2000 Å. These Rydbergs are superimposed on a broad "background" of $\pi\pi^*$ transitions. Up to now no fluorescence from Rydberg states of polyatomic molecules has been reported. The 1997 Å $n=3$ Rydberg of anthracene reveals fluorescence with a quantum yield of $\sim 5\%$. This fluorescence originates from internal conversion $R \rightsquigarrow S_1$ followed by $S_1 \rightarrow S_0$ emission, as documented by the spectral distribution of the dispersed fluorescence.
- 7.C Intramolecular Relaxation of Rydberg States. Information on intramolecular dynamics of extravalence excitations of benzene was obtained from lineshape analysis. The lineshape of the $^3P_{xy}(0)$ Rydberg is Lorentzian, whose homogeneous width result in the lifetime $\tau = 0.19 \pm 0.02$ psec for C_6H_6 and $\tau = 0.22 \pm 0.02$ psec for C_6D_6 . Semiquantitative information on the lifetimes of some Rydbergs of anthracene was obtained, which fall in the range of ~ 0.1 psec. These lifetime data imply that (i) the relaxation of the Rydberg is characterized by moderate energy gap(s), and (ii) the electronic relaxation rate of the Rydberg is considerably less efficient than that of the intravalence excitation in the same energy domain.
- 7.D Interference Effects between Extravalence and Intravalence Molecular Excitations. We have searched for Rydberg-valence interference effects in large molecules, which are expected to be exhibited in asymmetric Fano-type lineshapes in absorption. For "isolated" Rydbergs, which are superimposed on a $\pi\pi^*$ transition in benzene, naphthalene and anthracene, the absorption lineshapes are symmetric Lorentzians. No line asymmetry and no antiresonances characteristic of Fano profiles were found in that case. The absence of interference effects in this case reveals the manifestation of random interstate coupling of R with the π^* manifold. The random coupling erodes all interference effects. The situation is different for nearly lying Rydbergs, where pronounced R-R-valence interference effects were observed in the absorption spectra of jet-cooled naphthalene in the spectral region 1600-1650 Å, providing information on the homogeneous contribution to high-energy molecular coupling phenomena.

- 7.E Rotational State Dependence of Intramolecular Dynamics. Rotational effects on interstate coupling are of considerable current interest. Absolute fluorescence quantum yields from photo-selected rotational states were measured for the electronic origins of the S_1 state of pyrazine. Strong rotational state dependence was observed providing novel information on interstate coupling for the intermediate level structure. This unique information cannot be extracted from time-resolved decay lifetimes.
- 7.F The Coupling between Intrastate Vibrational Energy Redistribution and Interstate Electronic Relaxation. We have documented some universal characteristics of the decay lifetimes and fluorescence quantum yields from the S_1 manifold of large molecules, which originate from the coupling between intrastate vibrational energy redistribution and interstate electronic relaxation. The time-resolved total fluorescence decay excited by a psec laser from the S_1 state of jet-cooled 9CN-anthracene exhibits nonexponential decay in the energy range $E_V = 1200-1740 \text{ cm}^{-1}$ above the S_1 origin, which does not originate from dephasing but rather manifests the effects of intrastate intermediate level structure for vibrational energy redistribution on intersystem crossing.
- 7.G Coriolis Rotation-Vibration Coupling and Intramolecular Dynamics. We have demonstrated that rotational effects play a central role on intramolecular vibrational energy redistribution in electronic-vibrational excitations of large molecules. Strong rotational effects on the fluorescence quantum yields from vibrational states (above 1000 cm^{-1}) in the S_1 manifold of 9-cyanoanthracene were observed, which demonstrate that Coriolis interactions serve as the dominant coupling leading to intramolecular vibrational energy redistribution (IVR). In contrast to common wisdom, which attributed IVR in large molecules to anharmonic interactions, we have shown that rotational effects play a central role strongly enhancing interstate electronic relaxation.
- 7.H Resonances in Mediated Intersystem Crossing. The mechanisms of direct and of mediated intersystem crossing from the first excited singlet manifold of anthracene and some of its derivatives were explored by the study of the internal and the external heavy atom effect on the fluorescence quantum yields. Pronounced mode selectivity was observed in the vibrational energy dependence of the emission quantum yield in 9-bromoanthracene and 9,10-dibromoanthracene.

- 7.I Fluorescence Quantum Yields for Highly-Excited States of Large Molecules. Fluorescence quantum yields Y from high electronic excitations of naphthalene, anthracene and tetracene in the energy range 5.0-6.5 eV have been recorded. Y exhibits an exponential dependence on the excess vibrational energy with the slope decreasing with increasing size of the molecule, i.e., the vibrational density of states. These data are characteristic of internal conversion from S_1 to S_0 . These results are of interest regarding recent astrophysical implications of high-energy photophysics of large aromatic hydrocarbons in outer space.
- 7.J Photoisomerization Dynamics of Trans-Stilbene and of Cis-Stilbene. Time-resolved fluorescence lifetimes from photoselected states of trans-stilbene were recorded by the techniques of picosecond spectroscopy in jets using a mode-locked dye laser and a fast photon counting system. Decay lifetimes as short as 100 ± 30 psec were recorded. Extensive information on the energy dependence of the isomerization rates of alkyl stilbenes was obtained, providing information on the role of intramolecular vibrational distribution on the photochemistry in an isolated molecule. The absorption spectrum of jet-cooled cis-stilbene is broad and no vibrational structure could be resolved due to the congestion of broadened low-frequency vibrational excitation. From the low quantum yield $Y \leq 2 \times 10^{-4}$ we infer a S_1 lifetime of $\tau \leq 0.4$ psec, which indicates ultrafast relaxation of this molecule.
- 7.K Photoisomerization Dynamics of Alkyl Substituted Trans-Stilbene. A central issue pertaining to isolated-molecule photochemistry involves the role of intramolecular vibrational relaxation in determining intramolecular dynamics. We have attempted to increase the density of vibrational states by alkyl substitution of trans-stilbene and have explored the isomerization dynamics by picosecond time-resolved spectroscopy. We have obtained the counter-intuitive result that alkyl substitution of trans-stilbene enhances the photoisomerization rates, while general arguments based on the role of IVR and the implications of statistical theories indicate that the rate should be retarded. The results can be accounted for by the modification of the molecular parameters, i.e., threshold energy, by alkyl substitution.

- 7.L Energy-Resolved Photoisomerization Rates. The dynamics of the S_1 and S_2 electronically excited singlet states of diphenylbutadiene was interrogated by fluorescence quantum yield measurements over the very broad energy domain of 0-7500 cm^{-1} above the (false) S_1 origin. The issues of the lack of mode selectivity and the applicability of statistical theories for the description of isolated-molecule photochemistry were explored.
- 7.M van der Waals Complexes of Porphyrins. Excited-state energetics and dynamics of large complexes consisting of porphyrins bound to rare-gas atoms were explored. Detailed spectroscopic information on the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the free-base porphine-Ar complex was obtained, providing insight into the structure of this complex as well as resulting in a novel mechanism for microscopic solvent shifts induced by configurational distortions, which are due to complexing.
- 7.N Coupling between Intramolecular and Intermolecular Nuclear Motion in Complexes. Intermolecular vibrations of large van der Waals complexes, which involve the motion of the ligand relative to the large molecule, provide an analogue for surface vibrational motion in a finite system and constitute the precursors of phonon modes in condensed phases. Information on the coupling between intermolecular and intramolecular vibrational motion was obtained for the trans-stilbene-Ar complex.
- 7.O Analogies between Large van der Waals Molecules and Microsurfaces. The binding of rare-gas (R) atoms to large aromatic molecules (M) on the one hand, and to the basal plane of graphite on the other hand, represent two extremes of the interaction of R atoms with ordered arrays of sp^2 hybridized carbon atoms. We have explored the analogies between the characteristics of large van der Waals $\text{M} \cdot \text{R}_n$ complexes and R atoms on graphite surfaces, focusing on structure, packing, orientational registry effects and the nuclear motion of R adsorbates on finite microsurfaces. The elucidation of the structure, energetics and nuclear dynamics of large $\text{M} \cdot \text{R}_n$ complexes rests on semi-empirical model calculations of potential surfaces. These provide a quantitative account of the geometry, the existence of isomers, the dissociation energies and the frequencies of out-of-plane and in-plane vibrational modes for large amplitude intermolecular nuclear motion.

- 7.P Electron Localization in Clusters. Small clusters exhibit unique physical and chemical phenomena, which are both of fundamental and technological significance, and provide ways and means to explore the "transition" from molecular to condensed-matter systems. We have provided a theoretical study of the structure, energetics and dynamics of an excess electron interacting with an alkali-halide cluster, which was explored by the quantum path integral molecular dynamics method. These studies establish various compositional, structural and size dependence of bulk and surface localization mechanisms of the dynamic process induced by electron attachment.
- 7.Q Vibrational Predissociation Induced by Exciton Trapping in Rare-Gas Clusters. The dynamics of exciton trapping, vibrational energy transfer and vibrational predissociation in an electronically excited state of Ar_{13} clusters was explored by classical molecular dynamics. This study constitutes an application of this technique for the dynamics of electronically excited states of large systems. New mechanisms of ultrafast (~ 10 psec) vibrational energy flow induced by short-range repulsion were documented. In these systems vibrational energy redistribution does not occur and mode selective excitation prevails. In small ($n=13$) clusters the consequences of vibrational energy flow results in reactive vibrational predissociation, leading to the "evaporation" of Ar atoms for the cluster. In larger ($n=55$) clusters a transition from molecular-type reactive behavior to nonreactive vibrational relaxation, which is characteristic of condensed phases, was exhibited.

8. PUBLICATIONS

The following manuscripts, supported by this research grant, were prepared and submitted for publication:

- (1) A. Amirav and J. Jortner
Vacuum Ultraviolet Absorption Spectroscopy in Supersonic Expansions
J. Chem. Phys. (Communication) 82, 4378 (1985)
- (2) A. Amirav and J. Jortner
Rotational and Vibrational State Dependence on Intramolecular Coupling and Dynamics in the S_1 State of Pyrazine
J. Chem. Phys. (in press)
- (3) J. Troe, A. Amirav and J. Jortner
Energy-Resolved and Thermalized Photoisomerization Rates of Diphenyl-Butadiene
Chem. Phys. Letters 115, 245 (1985)
- (4) A. Amirav, M. Sonnenschein and J. Jortner
Interstate Coupling and Dynamics of Excited Singlet States of Isolated Diphenylbutadiene
Chem. Phys. 102, 305 (1986)
- (5) U. Even, Z. Berkovitch-Yellin and J. Jortner
Electronic Excitations of the Free-Base Porphine-Ar van der Waals Complex
Canad. J. Chem. (C. Sandorfy-Special Issue) 63, 2073 (1985)
- (6) D. Bahatt, U. Even and J. Jortner
Coupling between Intramolecular and Intermolecular Nuclear Motion in a Large van der Waals Complex
Chem. Phys. Letters 117, 527 (1985)

8. PUBLICATIONS (cont'd)

- (7) Klaus Rademann, Uzi Even, Shlomo Rozen and J. Jortner
Photoisomerization Dynamics of Alkyl Substituted Stilbenes
in Supersonic Jets.
Chem. Phys. Lett. 125, 5-11 (1986)

- (8) A. Amirav, J. Jortner, S. Okajima and E. C. Lim
Manifestations of Intramolecular Vibrational Energy
Redistribution on Electronic Relaxation in Large Molecules
Chem. Phys. Letters (in press)

- (9) U. Landman, D. Scharf and J. Jortner
Electron Localization in Alkali-Halide Clusters
Phys. Rev. Letters 54, 1860 (1985)

- (10) Dafna Scharf, Uzi Landman and Joshua Jortner
Energetics and Dynamics of Clusters
Proc. of the Int'l School of Physics "Enrico Fermi", Italy,
1986, in: Advances in Chemical Reaction Dynamics (D. Reidel
Publishing Company)

- (11) D. Scharf, U. Landman and J. Jortner
Vibrational Predissociation Induced by Exciton Trapping in
Inert-Gas Clusters
Chem. Phys. Letters 126, 495-500 (1986)

- (12) Dafna Scharf, Uzi Landman and J. Jortner
Surface States of Electrons and Alkali-Halide Clusters
Proc. of the 19th Jerusalem Symposium, Israel, 1986. Eds
J. Jortner and B. Pullman (D. Reidel Publishing Company,
Holland, 1986)

- (13) Samuel Leutwyler and Joshua Jortner
The Adsorption of Rare-Gas on Microsurfaces of Large
Aromatic Molecules
J. Phys. Chem.
- (14) Dafna Scharf, Uzi Landman and Joshua Jortner
Atomic and Molecular Quantum Mechanics by the Path
Integral Molecular Dynamics Method
Chem. Phys. Letters
- (15) A. Amirav and Joshua Jortner
Rotation, Vibration and Electronic Relaxation
Proc. of the CECAM Conference, Orsay, France, 1986
- (16) A. Amirav and J. Jortner
Resonances in Mediated Intersystem Crossing of Jet-
Cooled Anthracene Derivatives
Chem. Phys. Letters
- (17) A. Amirav, J. Jortner, M. Terazima and E.C. Lim
Rotational Effects on Intramolecular Radiationless
Transitions in a Large Molecule
Chem. Phys. Letters 132, 335-340 (1986)

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